

Density and T_g of glasses of the As-Al-Te system

S. MAHAD EVANA, GIRIDHAR

Materials Science Division, National Aeronautical Laboratory, Bangalore 560 017, India

Results of measurement of the density and the glass transition temperature (T_g) on 25 glass compositions of the As-Al-Te system are reported and discussed. A linear increase of density and a decrease of T_g are seen with increasing As content across the AsAlTe_4 - As_2Te_3 tie-line compositions. In the density-composition and mean atomic volume-composition dependences for the $\text{As}_x\text{Al}_5\text{Te}_{95-x}$, $\text{As}_x\text{Al}_8\text{Te}_{92-x}$ and $\text{As}_x\text{Al}_{12}\text{Te}_{88-x}$ glasses, a change in slope is seen at the

and similar papers at core.ac.uk

provided by National A

chemical ordering are obscured, instead, the effects of topological nature emerge, with changes in slope at the topological thresholds of $Z \approx 2.40$ and $Z \approx 2.67$. The results further indicate that the dependence of mean atomic volume v on Z is controlled by the Te content in these glasses. Due to this, the generally observed features in the dependence of v on Z for chalcogenide glasses, namely a minimum in v for $Z \approx 2.40$, a peak in v for $Z \approx 2.67$ and a decrease of v for $Z > 2.67$, are suppressed.

1. Introduction

The As-Al-Te glass system is important due to the switching effect observed in bulk glasses of this system [1]. The glass formation in this system extends [2] up to about 20 at % Al and 35-75 at % Te, the rest being As (Fig. 1a). Though characterization studies on several random compositions [3] and structural data on some glasses [4, 5] have been reported, systematic variation of the properties with composition has not been investigated for this system.

The compositions of the glasses prepared for the present study are indicated in Fig. 1b and listed in Table I. Based on the existence of the ternary compound AsAlTe_4 [6], which is also easily obtained in the glassy state, six of the compositions studied presently were chosen along the AsAlTe_4 - As_2Te_3 tie-line. The study also covered glasses of families with Al at 5, 8, 10, 12 and 16.67 at %. One glass composition from each of these families is also a member of the AsAlTe_4 - As_2Te_3 tie-line and thus forms the so-called "stoichiometric" or tie-line composition of the corresponding family. With the tie-line composition of each family as reference, glasses with As content higher than that of the corresponding tie-line composition can be referred to as the As-rich compositions, and glasses with As content lower than that of the corresponding tie-line composition as the Te-rich compositions of the respective families.

In this communication, the results of measurement of the density and glass transition temperature (T_g) of these glasses are presented; the observed features in the composition dependence of these properties are understood on the basis of the existing models [7-15] for network glasses.

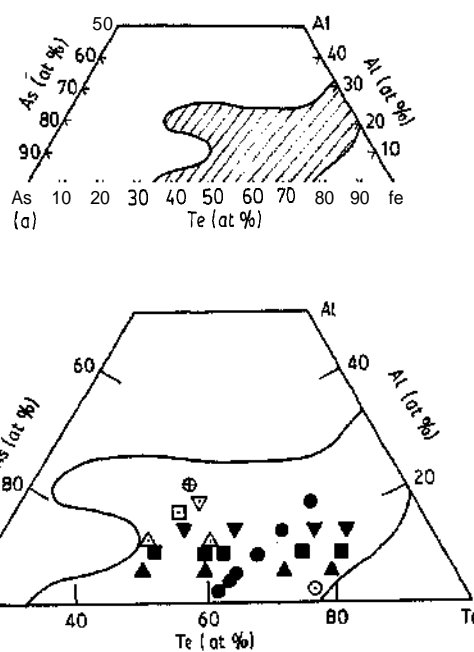


Figure 1 (a) The hatched portion indicates the glass-forming region of the As-Al-Te system [2]. (b) Glasses studied in the present work (with corresponding symbols used in the various figures): (●) Tie-line compositions, (▲) $\text{As}_x\text{Al}_5\text{Te}_{95-x}$, (○) $\text{As}_x\text{Al}_8\text{Te}_{92-x}$, (△) $\text{As}_x\text{Al}_{10}\text{Te}_{90-x}$, (□) $\text{As}_x\text{Al}_{12}\text{Te}_{88-x}$. Compositions are listed in Table I.

2. Experimental procedure

The glasses were prepared in fused silica ampoules by the standard melt-quenching method generally adopted for chalcogenide glasses. As Al reacts with fused silica at high temperatures, the preparations were done in graphitized fused silica ampoules.

TABLE I Data on d , v , T_g and Z of the As-Al-Te glasses studied

Sample No.	Composition (at %)			rf _{obs} (gcm)	3) ^b	ν (cm ³)	Z	T _g (K)
	As	Al	Te					
1 ^a	37.2	2	60.8	5.538 ± 0.001	19.14	2.506	386	
2	23	2	75	5.623 ± 0.002	20.16	2.403	367	
3 ^a	34.4	4	61.6	5.493 ± 0.008	19.20	2.540	390	
4	47.5	5	47.5	5.274 ± 0.001	18.50	2.670	419	
5	38	5	57	5.395 ± 0.009	19.01	2.595	399	
6 ^a	33	5	62	5.465 ± 0.005	19.25	2.557	392	
7	26	5	69	5.520 ± 0.006	19.71	2.505	379	
8	19	5	76	5.546 ± 0.005	20.30	2.456	370	
9	45	8	47	5.162±0.014	18.57	2.734	426	
10	37	8	55	5.296 ± 0.009	18.89	2.671	409	
11	34	8	58	5.336± 0.019	19.05	2.647	404	
12 ^a	28.8	8	63.2	5.401± 0.019	19.33	2.608	396	
13	22	8	70	5.446 ±0.008	19.83	2.558	383	
14	16	8	76	5.502 ± 0.005	20.20	2.516	373	
15	46	10	44	5.004 ± 0.006	18.65	2.799	440	
16	35	10	55	5.253 ± 0.001	18.87	2.711	415	
17	38	12	50	5.096 ± 0.014	18.74	2.790	432	
18	30	12	58	5.269 ± 0.004	18.93	2.727	415	
19 ^a	23.2	12	64.8	5.323 ± 0.002	19.41	2.676	402	
20	18	12	70	5.353 ± 0.002	19.77	2.638	392	
21	13	12	75	5.433 ± 0.005	20.00	2.603	382	
22	38	14	48	5.065 ± 0.003	18.46	2.846	438	
23	33.33	16.67	50	5.004 ± 0.019	18.64	2.883	448	
24 ^a	16.67	16.67	66.67	5.198 ± 0.009	19.63	2.756	407	
25	33	20	47	4.907 ± 0.005	18.36	2.930	470	
a ^c	20	2	78	5.625	—	2.364	364	
b	25	2	73	5.600	20.07	2.417	—	
c	30	2	68	5.575	19.69	2.453	—	
d	22	5	73	5.536	20.04	2.477	—	
e	30	10	60	5.325	—	2.672	—	
f	43	10	47	5.100	—	2.774	—	

^aTie-line compositions.^bThis column gives the mean value of the density along with the experimentally observed scatter for the various compositions.^cThe data for compositions a to f are interpolated from the data of Fig. 2.

Appropriate quantities (6-8 g total) of pure elements (99.999%, As and Te obtained from Atomergic Chemmetals Corp., USA and Al from Johnson Matthey, USA) were weighed and sealed under a vacuum of 10^{-5} torr. The ampoules were then heated in a rotary furnace (for purposes of homogenization) at 800 °C for 8 h and quenched in iced water to obtain the glasses. The amorphous nature of the various compositions was confirmed by recording their powder X-ray diffractograms ($\text{CuK}\alpha$).

Densities were determined by the hydrostatic method using the density kit supplied along with the microanalytical balance used (Sartorius, model A 200 S). Deionized water was used as the immersion fluid and utmost care was exercised to avoid formation of any air bubbles around the sample which can affect the measured density. The error in measurement was further reduced by choosing large (typically 1 g) samples for measurement. Densities were measured on four to six samples from each batch preparation; the mean value obtained for these samples is indicated in Table I along with the experimentally observed scatter for the various compositions. The maximum scatter in the density value for different samples of any given composition ranged from 0.02 to 0.2% for most of the compositions and up to 0.4% in a few cases (Table I).

A scatter of similar magnitude was observed from measurements on different batch preparations of specified compositions.

After the routine calibration, a Perkin Elmer DSC-2 differential scanning calorimeter (DSC) was used for recording the thermograms to determine T_g . Using the standard procedure [16], T_g was identified as the temperature corresponding to the intersection of the two linear portions adjoining the transition elbow of the DSC trace. The T_g values indicated (Table I) are those obtained at a heating rate of 10 K min^{-1} , on samples which were annealed (by holding at temperature of about 10 K higher than the respective T_g for 15 min) and then cooled through the transition region at a rate of 10 K min^{-1} .

3. Results

The densities of the various compositions along with the observed scatter and their mean atomic volume (v) are all listed in Table I. The mean value of d has been used for evaluating v for the various compositions.

Fig. 2 shows the variation of density with composition. A linear increase of density with increasing As (i.e. As_2Te_3) content is seen for the tie-line compositions (line AA through filled circles in Fig. 2). A change

in slope in the dependence of density on composition is seen at the corresponding tie-line composition for the families investigated.

The linear dependence of the density of the Te-rich glasses of the various families, when extrapolated to the corresponding Te (100 at %) point, give a value of $5.725 \pm 0.005 \text{ g cm}^{-3}$ for the density of glassy Te. Amorphous Te cannot be obtained in bulk form and so its density value is not available. The present value of 5.725 g cm^{-3} , assuming a generally observed increase of about 10% in density on crystallization of many chalcogenide glasses, gives a value of 6.29 g cm^{-3} for crystalline Te, in good agreement with the value of 6.24 g cm^{-3} for Te. A value of 5.86 g cm^{-3} has been inferred for the density of glassy Te from data on the As-Te system [17].

A similar extrapolation of the density of As-rich glasses to the pure As (100 at %) end shows some interesting features. The density data points of the $\text{As}_x\text{Al}_5\text{Te}_{95-x}$ family, when extrapolated to the pure As end (broken line extension to 100 at % of As, Fig. 2) gives a value of 4.695 g cm^{-3} for the density of amorphous As, which is in excellent agreement with the reported value of 4.70 g cm^{-3} [18] for amorphous As. For the $\text{As}_x\text{Al}_8\text{Te}_{92-x}$ family (filled squares in fig. 2), the density data of As-rich glasses up to about 37 at % As fall along the line joining the density of the corresponding tie-line composition with the density of As. For the $\text{As}_x\text{Al}_{10}\text{Te}_{90-x}$ glasses (open triangles), the deviation sets in around the composition $\text{As}_{30}\text{Al}_{10}\text{Te}_{60}$. Thus for families with a progressive increase in Al content (i.e. as one moves from top to bottom along the line AA), there is a reduction in the As content of the compositions up to which the density data fall along the line joining the density of the corresponding tie-line composition with that of As.

For the tie-line compositions (Fig. 3a), a linear decrease of v is indicated with increasing As content. The data for v of the individual families (Fig. 3b) reflect the dependence of the densities of these glasses (Fig. 2). A change in slope is seen at the respective tie-line compositions of the various families, followed by another change in slope for the families with Al at 8, 10 and 12 at % at compositions which have As at 37, 30 and 28 at %.

In the T_g -composition data (Fig. 4a), a linear decrease of T_g with increasing As content is seen for the AsAlTe_4 - As_2Te_3 glasses; this dependence, when extrapolated to 40 at % As, agrees well with the reported [17, 19, 20] T_g of As_2Te_3 . For the individual families, an increase of T_g with increasing As content is observed.

4. Discussion

4.1 Existing models and expected features

In this section, salient features of existing models [15], which are helpful in understanding the observed features, are briefly summarized. Earlier attempts at understanding the features seen in the composition dependence of various properties of chalcogenide glasses were based on the chemically ordered

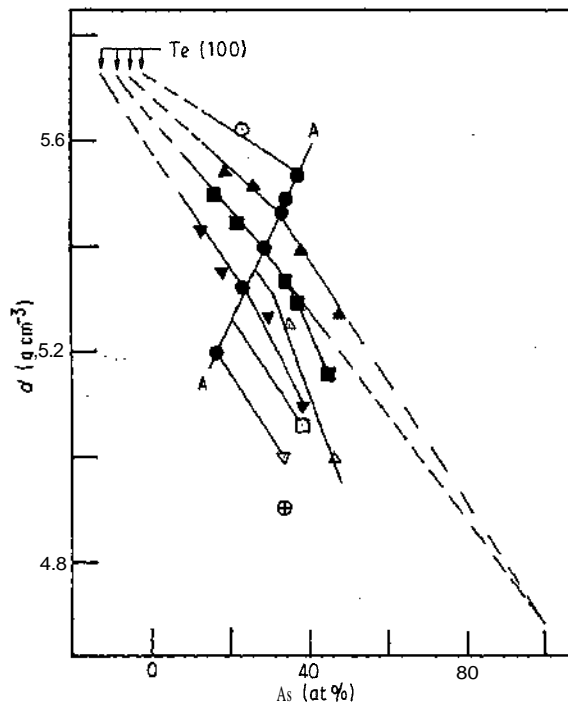


Figure 2 Density versus composition data for the various glasses. The symbols have the same meaning as in Fig. 1b. The line AA is through the tie-line compositions. Extrapolation of the density of Te-rich/As-rich glasses of the various families to the respective Te (100%)/As (100%) points are also indicated.

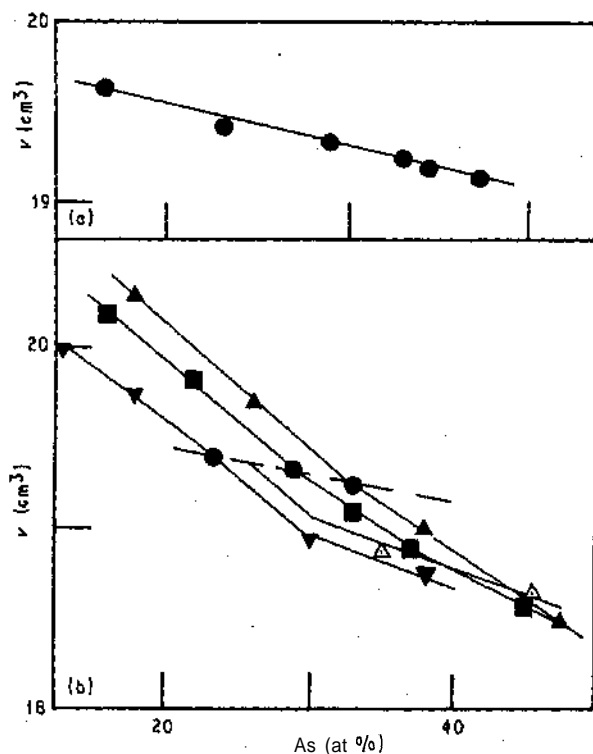


Figure 3 (a) Variation of ν with As content for the tie-line compositions, (b) variation of ν with composition for the various families of glasses with Al at 5, 8, 10 and 12 at %. Symbols as in Fig. 1b.

Network Model (CONM) [7, 8, 21-23]. In the CONM, the formation of heteropolar bonds is favoured over the formation of homopolar bonds; the glass structure is pictured to be made up of cross-linked structural units of stable chemical compounds

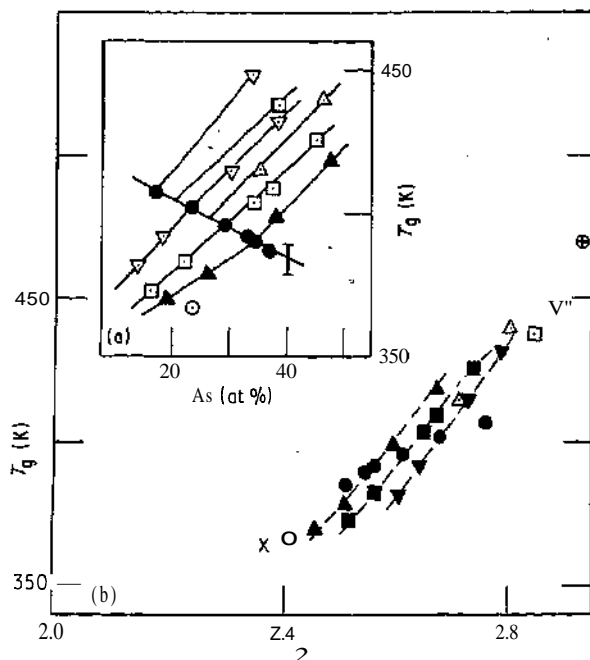


Figure 4 (a) T_g versus composition for the various families of As-Al-Te glasses. Extension of the data of the tie-line compositions (●) to the data of As_2Te_3 glass at 40 at. % As is also indicated. (b) T_g versus Z for the As-Al-Te glasses. The broken lines show the dependence of the individual families with Al at 5, 8 and 12 at %. Symbols as in Fig. 1b.

and then an excess, if any, of the elements [7]. Due to the effects of chemical ordering, in the composition dependence of various properties, specific features such as an extremum or change of slope or kink are seen at the tie-line compositions which can be considered to be made up of cross-linked structural units consisting of only heteropolar bonds.

The topological models developed subsequently [11–15] have found wide acceptance in understanding the features observed in the composition dependence of various properties of network glasses. In these models, the properties are discussed in terms of the average coordination number Z . Two topological thresholds at $Z \approx 2.40$ and $Z \approx 2.67$ are indicated in several glass systems [15], Ge-Se and As-Se being typical examples.

In the constraints models and developments thereof [11–14], by equating the number of operative constraints to the number of degrees of freedom, the Z of the most stable glass is shown to be ≈ 2.40 ; at $Z \approx 2.40$, the glass network has a mechanical threshold or critical point, at which the network moves over from an elastically floppy type to a rigid type.

The features observed at $Z \approx 2.67$ have been understood using the structural transitions model, in which the dimensionality of the network changes from a value of unity corresponding to the chalcogen to higher values as As/P/Ge/Si etc. are added [15]. The threshold at $Z \approx 2.67$, also established by topological considerations using medium-range structures, is attributed to the transition from an essentially layered structure to a three-dimensional network arrangement due to cross-linking.

The variation of v with Z has been discussed for the As-Se, As-S, Ge-Se, Ge-S and Ge-As-Se systems

[15]. In these systems, the overall dependence is a reduction of v with increasing Z . In addition, features of a minimum in v at $Z \approx 2.40$ and a peak in r for $Z \approx 2.67$ are seen due to the two topological effects mentioned above. For $Z > 2.67$, a reduction in v occurs to the v of As (at $Z = 3$) or the v of Ge (at $Z = 4$). The minimum in v at $Z \approx 2.40$ is understood [15] by conceiving that the most stable glass should have a minimum in v ; the decrease of v for $Z > 2.67$ is traced to a transition to a three-dimensional network arrangement. The observed increase in v from $Z = 2.40$ to $Z = 2.67$ is accounted for in this model in the light of a two-dimensional layer structure that is proposed for these glasses in this range of Z . Using X-ray diffraction data, the layer separation in compositions with Z from 2.40 to 2.67 is related to the expansion of the interlayer distance. In this context, the composition change in this region is regarded as an application of "negative pressure". This enhances the interlayer distance, thereby increasing volume. While atomic volume is primarily governed by layer separation, it can be modified by secondary effects like structural randomness.

4.2. Variation of d and v with composition

In the variation of density and v with composition for the various families of the As-Al-Te glasses, a change in slope was seen (Figs 2 and 3, respectively) at the tie-line compositions of the corresponding families. Based on the CONM model [7–10] the glass structure can be visualized to be made up of cross-linked units of $AsAlTe_4$ and As_2Te_3 with excess As or Te dispersed among these units. The features seen at the tie-line compositions (which are made up of cross-linked units of $AsAlTe_4$ and As_2Te_3 , only with neither As nor Te in excess) is due to this chemical ordering effect.

Apart from a change in slope at the tie-line compositions (along the line AA in Fig. 2) another change in slope was seen in the density–composition and v –composition data for the various families. The reason for this change in slope is due to the topological "structural transition" occurring in these glasses, which is discussed in the next section.

4.3. Variation of d with Z

For analysing d and v in terms of the topological models, the Z values of these glasses were evaluated using the standard procedure [24]. The coordination of As, Al and Te used in the evaluation of Z were obtained from the results of structural data on these glasses [4, 5] and also on glasses of the related Al-Te [1] and As-Te [25] systems. The following conclusions have been drawn from these studies.

(i) Al has tetrahedral coordination in all these glasses.

(ii) Based on the low value of Al-Al bond energy and the low atomic percentage of Al in these glasses, the formation of Al-Al bonds is negligible.

(iii) In the bonding scheme, each Al atom takes one electron from one of the As or Te atoms which

surrounds it. The atom which gives the electron becomes fourfold or threefold coordinated depending on whether it is an As or a Te atom; every atom in the tetrahedra vertex provides 1/4th of an electron to the Al atom in a probabilistic sense.

(iv) Apart from those Te atoms bound to Al atoms which have threefold coordination, an additional fraction of about $0.2 \cdot x \%$, where x is the atomic percentage of Te in the glass, is also found in threefold coordination.

(v) Based on the approximately equal values of the Al-As and Al-Te bond energies, the numbers of Al-As and Al-Te bonds are proportional to the relative concentrations of As and Te in the corresponding glass composition.

Table I lists the Z values of the various compositions, evaluated using the conclusions summarized above. Fig. 5 shows the d - Z data for these glasses, in which extensions to the d of Te at $Z = 2$ and to that of As at $Z = 3$ are also indicated. The data of Fig. 5 indicate a change in slope at $Z \approx 2.67$. With the limited data available at low Z , a change of slope is seen at $Z \approx 2.43$ also. However, generating data points at lower values of Z between 2.0 and 2.4 was precluded in this system by the boundary of the glass-forming region. The change in slope occurring at the topological thresholds of $Z \approx 2.40$ and $Z \approx 2.67$ are due respectively to the floppy-to-rigid transition and the "structural transition" occurring in network glasses which are summarized in section 4.1. In the d - Z data, the effects of chemical ordering (which was seen as a change in slope at the tie-line compositions in the d -composition data of Fig. 2) is obscured. Corresponding to this transition at $Z \approx 2.67$ (Fig. 4), changes in slope were seen in the d -composition data (Fig. 2) also at the compositions which have Z values of 2.67 (Table I).

4.4. Variation of ν with Z

The ν - Z data for the As-Al-Te glasses are shown in Fig. 6. Due to the large scatter in the data points at any Z , it is not possible to infer any regular dependence of ν on Z . At any specified Z , compositions with higher Te content have larger volumes, suggesting a correlation between the ν and the Te content. That this is indeed the case is seen from the data in the inset of Fig. 6. A monotonic increase of ν with Te content is seen, with the dependence extrapolating well to the ν of Te at 100 at % Te and to the ν of As at 0 at % Te.

In the systems whose ν - Z dependences were discussed in section 4.1, the atomic radii of the constituent atoms As, Se, Ge (0.122, 0.117 and 0.126 nm, respectively) are approximately the same at 0.122 nm. In the As-Al-Te system studied presently, the Te atoms have large radii (0.138 nm) compared to those of As and Al (0.125 nm). In the structural transitions of model [15] already discussed in section 4.1, in the region of Z between 2.40 and 2.67, ν is determined by the interlayer separation of the two-dimensional layer structure proposed for these glasses. The larger Te atoms which determine the interlayer separation thus

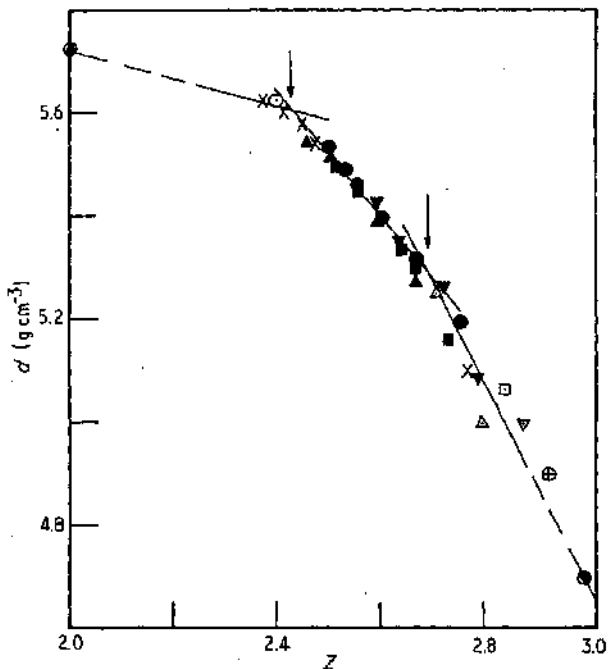


Figure 5 Density versus Z for the various glasses studied; (X) values interpolated from Fig. 2 (also listed in Table I). Extrapolations to the densities of 100% Te and As are also shown. Clear changes in slopes are seen at $Z = 2.43$ and also at $Z = 2.67$. Other symbols as in Fig. 1b.

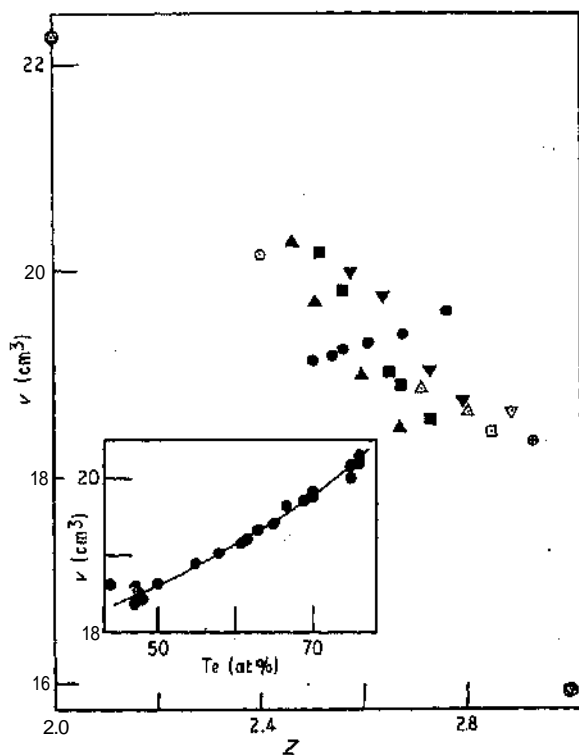


Figure 6 ν versus Z for the various glasses. The ν of Te at $Z = 2$ and of As at $Z = 3$ are also included. The inset shows ν as a function of Te content in the glasses. Symbols as in Fig. 1b.

control the resultant volume. The features of a minimum in ν at $Z \approx 2.40$ and the peak in ν at $Z \approx 2.67$ in the ν - Z dependence, seen in systems whose constituent atoms have approximately the same radii, are thus suppressed in this system in which the constituent atoms differ largely in atomic radii.

4.5. Dependence of T_g on composition and Z
It is known that several complicating factors determine the T_g of a glass [24]. Using the empirical T_g-E_g-C correlation [26] (where E_g and C are the optical gap and the connectedness, respectively) that is generally used to understand the T_g behaviour of chalcogenide glasses, it is possible to qualitatively rationalize the observed (Fig. 4) dependence of T_g on composition and Z.

In the T_g-E_g-C correlation an increase of T_g is indicated with increase of connectedness, i.e. average coordination number Z. In chalcogenide glass systems, the optical band gap is twice the activation energy of electrical conductivity, ΔE [27]. Conductivity data on several As-Al-Te glasses indicate [28] that $2A\epsilon$ does not drastically alter for these glasses; in the overall observed change in this parameter from 0.70 to 0.90 eV, $A\epsilon$ decreases with increasing Al content. The Z of these glasses increases with increasing As content (Table I). The observed increase of T_g with increasing Al content for the tie-line compositions (closed circles in Fig. 4a) can be qualitatively traced to the larger effect of Z on T_g than that due to the change in ΔE . For the individual families, the increase of T_g with increase of As content is traceable to the increase of Z (Table I).

The T_g-Z data (Fig. 4b) do indicate, as expected, an overall increase of T_g with increasing Z. When the data of individual families are considered at any specified Z, it is seen that the families with higher Al content have lower T_g . This is attributable to the decrease of $A\epsilon$ with increasing Al content in the glasses. This results in the spread or "width" seen in the overall dependence of T_g on Z (Fig. 4b).

5. Conclusions

The results of measurement of the density and T_g of 25 glass compositions of the As-Al-Te system are reported and discussed. A linear increase in density and a decrease in T_g are seen with increasing As content across the $AsAlTe_4-As_2Te_3$ tie-line compositions.

When examined as a function of composition, the density and ν of the various families of glasses indicate a change in slope at the respective tie-line compositions due to chemical ordering. There is another change in slope at the compositions which have $Z \approx 2.67$, which is due to the topological transition occurring at this value of Z.

When examined as a function of Z, the effects of chemical ordering are obscured and those due to the topological nature of the networks emerge. In the $d-Z$ data changes in slope are seen for $Z = 2.43$ and $Z = 2.67$ which are respectively due to the floppy-to-rigid transition and the "structural transition" occurring in network glasses.

The results further indicate that the dependence of ν on Z is determined by the Te content in these glasses due to the larger atomic radius of Te. Because of this some expected features at $Z \approx 2.40$ and $Z \approx 2.67$ in the dependence of ν on Z are suppressed.

The T_g behaviours of these glasses are rationalized on the basis of their band gap and Z values.

Acknowledgement

Thanks are due to Dr A. K. Singh for helpful discussions.

References

1. A. ALEGRIA, A. ARRUBARRENA and F. SANZ, *J. Non-Cryst. Solids* 58 (1983) 17.
2. J. A. SAVAGE, *ibid.* 11 (1972) 121.
3. Z. U. BORISOVA, in "Glassy Semiconductors" (Plenum, New York, 1981) Ch. 7.
4. J. J. DEL VAL, L. ESQUIVIAS, P. L. OLANO and F. SANZ, *J. Non-Cryst. Solids* 70 (1985) 211.
5. L. ESQUIVIAS and F. SANZ, *ibid.* 70 (1985) 223.
6. A. WEISS, *Naturwissenschaften* 47 (1960) 495.
7. G. LUCOVSKY, F. A. GALEENER, R. H. GEILS and R. C. KEEZER, in "Structure of Non-Crystalline Solids", edited by P. H. Gaskell (Taylor & Francis, London, 1977) p. 127.
8. G. LUCOVSKY, R. J. NEMANICH and F. L. GALEENER, in Proceedings of 7th International Conference on Amorphous and Liquid Semiconductors, Edinburgh, 1977, edited by W. E. Spear (Institute of Physics, Bristol, 1978) p. 130.
9. F. BETTS, A. BEINENSTOCK and S. R. OVSHINSKY, *J. Non-Cryst. Solids* 4 (1970) 387.
10. G. LUCOVSKY, F. L. GALEENER, R. C. KEEZER, R. H. GEILS and H. A. SIX, *Phys. Rev.* B10 (1974) 5134.
11. J. C. PHILLIPS, *J. Non-Cryst. Solids* 34 (1979) 153.
12. *Idem*, *ibid.* 43 (1981) 37.
13. M. F. THORPE, *ibid.* 57 (1983) 355.
14. J. C. PHILLIPS and M. F. THORPE, *Solid State Commun.* 53 (1985) 699.
15. K. TANAKA, *Phys. Rev.* 39B (1989) 1270.
16. C. T. MOYNIHAN, A. J. EASTEAL, J. WILDER and J. TUCKER, *J. Phys. Chem.* 78 (1974) 2673.
17. J. CORNET and D. ROSSIER, *J. Non-Cryst. Solids* 12 (1973) 61.
18. C. T. WU and H. L. LUO, *ibid.* 18 (1975) 21.
19. L. STOURAC, A. ABRAHAM, A. HRUBY and M. ZAVETOVA, *ibid.* 8-10 (1972) 353.
20. C. H. SEAGER and R. K. QUINN, *ibid.* 17 (1975) 386.
21. C. H. HURST and E. A. DAVIS, in "Amorphous and Liquid Semiconductors", Vol. 1, edited by J. Stuke and W. Brenig, (Taylor & Francis, London, 1974) p. 349 and references therein.
22. P. S. L. NARASIMHAM, A. GIRIDHAR and S. MAHADEVAN, *J. Non-Cryst. Solids* 43 (1981) 365.
23. A. GIRIDHAR, P. S. L. NARASIMHAM and S. MAHADEVAN, *ibid.* 43 (1981) 29.
24. S. R. ELLIOTT, in "Physics of Amorphous Materials" (Longman, London, 1983) Ch. 2.
25. J. CORNET and D. ROSSIER, *J. Non-Cryst. Solids* 12 (1973) 85.
26. J. P. DENEUFVILLE and H. K. ROCKSTAD, in Proceedings of 5th International Conference on Amorphous and Liquid Semiconductors, Garmisch-Partenkirchen edited by J. Stuke and W. Brenig (Taylor & Francis, London, 1974) p. 419.
27. E. A. OWEN, *Key Eng. Mater.* 13-15 (1987) 443.
28. Z. U. BORISOVA, in "Glassy Semiconductors" (Plenum, New York, 1981) Ch. 7.

Received 7 October 1991
and accepted 11 August 1992